

**Shell Oil Products U.S., Inc.
Shell Martinez Refinery
Martinez, California
CAD 009 164 021**



Protocol for the CO Boiler Health Risk Assessment

Revision 1



ENSR Corporation

November 2005 (revised from April 2005)

Document Number 05975-140-800

TABLE OF CONTENTS

1.0	Introduction	1-1
1.1	Project Background.....	1-1
1.2	Facility Location	1-1
1.3	Facility Contact Information	1-2
2.0	Description of Hazardous Wastes and Process Equipment.....	2-1
2.1	Description of CO Boilers.....	2-1
2.2	Tank 12038	2-2
2.3	Waste Feed Stream	2-2
3.0	Overview of HRA Approach.....	3-1
4.0	Emissions Information	4-1
4.1	Emission Sources	4-1
4.2	Compounds of Potential Concern (COPCs).....	4-1
4.3	Emission Rates	4-2
5.0	Air Dispersion Modeling.....	5-1
5.1	Air Dispersion Model.....	5-1
5.2	Meteorological Data	5-1
6.0	Exposure Assessment	6-1
6.1	Identification of Receptors	6-1
6.2	Identification of Exposure Pathways.....	6-1
6.3	Exposure Models	6-3
7.0	Dose-Response Assessment	7-1
8.0	Risk Characterization	8-1
8.1	Uncertainty Analysis	8-1
8.2	Discussion of Potential Ecological Impacts	8-1
9.0	References.....	9-1
Table 2-1	Typical Waste Feed Characteristics	2-3

Appendix A: Compounds to be Analyzed in the Upcoming Trial Burn

1.0 INTRODUCTION

1.1 Project Background

This document is a Protocol for conducting a Health Risk Assessment (HRA) for three carbon monoxide boilers (CO boilers) at the Shell Martinez Refinery (SMR) located in Martinez, California (U.S. EPA ID# CAD 009 164 021). The Protocol outlines the steps to be taken during the air dispersion modeling and risk assessment process.

SMR operates an oil refining and manufacturing complex which manufactures LPG, gasoline, intermediate fuels (jet and diesel), industrial fuels, asphalt, petroleum coke, sulfur and catalysts. SMR currently operates three carbon monoxide boilers (COBs) and storage tank 12038 that are addressed by the current Hazardous Waste Facility Permit (RCRA Part B Permit) issued by the California Department of Toxic Substances Control (DTSC).

As part of the RCRA Part B Permit renewal process, a Trial Burn will be conducted on one of the three identical CO boilers. Testing will be conducted to demonstrate compliance with anticipated permit conditions and to generate information for this HRA which is also required as a part of the RCRA Part B Permit renewal process. Details on the Trial Burn are provided in the Trial Burn Plan (ENSR, 2005). SMR proposes to conduct the Trial Burn under three boiler operating conditions to fully meet permit requirements and to establish new operating limits. Test Condition 1 is designed for system operation at minimum (~30-kVA) power input to the electrostatic precipitator (ESP). Test Condition 2 is designed for all risk-based testing while the unit is under normal operating conditions. Test Condition 3 is designed for system operation at a low firebox temperature, maximum firebox pressure, and maximum waste feed rate and will be used to demonstrate the destruction and removal efficiency (DRE). This HRA will be based on data collected in Test Condition 2, which evaluates typical facility operations and will collect data to determine the chemicals and their concentrations emitted by the COBs.

Previous risk assessments have been conducted for this facility and presented to DTSC to support the Part B Permit. The most recent one was conducted in 2000 by Bechtel Corporation (Bechtel, 2000). It is assumed that similar receptor and exposure locations identified in the Bechtel (2000) risk assessment will be used in this HRA.

1.2 Facility Location

SMR is located in Contra Costa County on the south shore of the Carquinez Strait, near the City of Martinez and north of the City of Concord. The Carquinez Strait feeds water from Suisun Bay to the San Francisco Bay and is a part of the San Francisco Bay-Delta Estuary Watershed, which receives flows from the Sacramento and San Joaquin river delta system and empties into the Pacific Ocean.

The State Water Resources Control Board (SWRCB) has designated beneficial uses of the Carquinez Strait as industrial service supply, a shipping waterway, recreation, commercial fishing, migration of aquatic organisms, spawning and fish reproduction, and an estuarine and wildlife habitat. The SWRCB does not consider the Carquinez Strait a source for the municipal drinking water supply.

The nearest fresh water body to the SMR is the Martinez Reservoir. This reservoir has the capacity for 270 acre-feet of water and is located approximately 0.2 miles south of the nearest SMR property boundary and about 0.5 miles southeast of the CO Boilers. The Martinez Reservoir is fed by the Contra Costa Canal, a 48 mile long water conveyance managed by the Contra Costa Water District (CCWD). Water from the Martinez Reservoir is pumped to the City of Martinez Water Treatment Plant. After treatment the water is supplied to the residents of Martinez as potable water.

Another fresh water reservoir, the Mallard Reservoir, is located approximately two miles east of SMR and just east of the current Tesoro refinery. The Mallard Reservoir provides raw water storage for the adjacent Bollman Water Treatment Plant, which supplies potable water to the central Contra Costa County. Water for the Mallard Reservoir is also supplied via the Contra Costa Canal and managed by the CCWD.

SMR is located in Contra Costa County, the ninth most populous county in California. The 2000 Census data indicated that total population for Contra Costa County was 948,816 persons. The US EPA Environmental Compliance History Online (ECHO) database indicates that the population within a radius of three miles from the approximate center of the SMR is 37,092 persons and the population in a radius of one mile surrounding SMR is 6,191 persons.

1.3 Facility Contact Information

General facility contact information includes:

Owner: Shell Oil Products US
Address: Shell Martinez Refinery
PO Box 711
3485 Pacheco Blvd.
Martinez, California 94553

U.S. EPA ID No: CAD 009 164 021

Facility Contact: Mr. Steven Overman, Senior Staff Engineer

Phone No.: (925) 313-3281

2.0 DESCRIPTION OF HAZARDOUS WASTES AND PROCESS EQUIPMENT

This section provides an overview of the hazardous waste stream and the permitted equipment used to handle the material. This equipment includes the three COB Boilers and Tank 12038.

2.1 Description of CO Boilers

This section provides a brief discussion of the CO Boilers at the Shell Martinez Refinery. A more detailed description of these units is included in Sections 2 and 3 of the Trial Burn Plan (ENSR, 2005)

SMR operates three CO boilers that are of identical design and operation. The purpose of the CO boilers is to recover energy in the form of steam from several process streams that are generated within the refinery. The boilers are each capable of producing 150,000 pounds per hour (lb/hr) of steam at 650 pounds per square inch, gauge (psig) pressure and 750°F. They are designated as sources S1507, S1509 and S1512 with the Bay Area Air Quality Management District (BAAQMD). Each boiler is a forced draft boiler and is operated continuously. Alcorn Combustion Manufacturing Company built the three boilers on the basis of a single design, without a model number.

The CO Boilers burn three gaseous fuels and one waste feed stream. The gaseous fuels which are normal byproducts of refinery processes are: Catalytic Cracking Unit (CCU) regenerator off gas; Flexigas® from the Flexicoker unit; and refinery fuel gas which contains gaseous hydrocarbon fractions from various refinery processes and is similar to natural gas. In addition, the CO Boilers receive and destroy wastewater treatment sludge that is generated at the SMR. This waste feed stream is a mixture of nonhazardous waste biosolids from the Effluent Treating Plant and dissolved nitrogen flotation (DNF) solids, which are a listed hazardous waste. SMR had been burning the wastewater solids in the CO Boilers prior to establishment of the RCRA hazardous waste program. These units became subject to Part B permitting when the US Environmental Protection Agency designated such wastewater solids as a hazardous waste.

The CO Boilers are well instrumented and air emissions from the CO boilers are tightly controlled. Each boiler is equipped with an automatic waste feed cutoff (AWFCO) system to prevent waste from being injected into the firebox when the boiler is running outside of permitted operating conditions. When a shutoff trip is activated, the waste feed shutoff valve closes quickly (there is approximately a three second delay) to stop the waste flow. Fuel, off gas, and air continue flowing into the firebox, and the boiler continues operating in a normal fashion. When operating conditions in the boiler have returned to within the permit limits, waste feed is again introduced into the firebox by resetting the solenoid that opens the shutoff valve and adjusting the flow controller to the desired flow.

Each of the three CO Boilers utilizes an electrostatic precipitator (ESP) to control particulate matter emissions. NO_x emissions are controlled by regulating CO Boiler operating conditions and by injecting urea downstream of the firebox in the heat recovery section. The urea reduces NO_x emissions by converting them to nitrogen.

The boiler operator inspects the boiler at least daily for fugitive emissions, leaks, spills, and signs of wear or tampering. Any leak or spill is cleaned up, and any emission point or worn equipment is corrected as soon as possible. Incidents and abnormal inspection results are noted in the operating log.

The boiler operator and utilities board operator attend to the boiler operation on a full time basis. They continuously check the operating data and make any necessary adjustments in control set points. Boiler operating data is collected and retained by the process control computer or strip charts.

In the event that an emergency shutdown of the boiler is initiated, the AWFCO system is activated and flow of waste feed is stopped immediately. Fuel and air are also shut off. Regenerator off gas will continue moving through the boiler and exhaust gas control system until the operator diverts the gas to the other two boilers.

The boiler is not equipped with a bypass (dump) stack. However, under extreme circumstances, regenerator off gas may be diverted upstream of the boiler to a bypass stack. Any leak or spill of waste feed and any effects on personnel or surroundings is reported to the appropriate Agencies, as required. Any leak or spill is promptly cleaned up.

2.2 Tank 12038

Tank 12038 is used to temporarily store the mixture of the hazardous waste DNF solids and the non-hazardous biosolids. Tank 12038 is a carbon steel double-walled tank with overall dimensions of 20 feet diameter and 20 feet high. The primary tank has a capacity of 47,750 gallons and the outer secondary containment tank has a capacity of 51,270 gallons. The tank system consists of a leak detection system, a nitrogen purge system, a vent absorber for odor and emissions control, a level indicator and alarm system, a mixer, flame arrestor, an overflow sump, and associated pumps, pipes, valves, and flanges.

2.3 Waste Feed Stream

The waste feed stream burned directly in the burners is a mixture of waste DNF solids and biosolids from the SMR Effluent Treatment Plant, which is a biological oxidation process. The DNF solids are a listed RCRA hazardous waste and have been assigned a Federal RCRA waste code of K048 and a California waste code of CWC 222. The biosolids stream is a non-hazardous waste. A representative summary for the waste feed analytical results is listed in **Table 2-1**. A more detailed compilation of waste feed analyses conducted over the past 10 years is presented in **Appendix A** of the Trial Burn Plan (ENSR, 2005).

Table 2-1 Typical Waste Feed Characteristics

Parameter	Units	Average	Minimum	Maximum
Physical Properties --				
High Heating Value	Btu/lb	408	< 100	1,240
Chlorine	%	0.09	0.042	0.45
Ash	%	0.69	0.26	1.38
Water Content	% wt.	95.7	90.0	98.7
Ultimate Analysis --				
Carbon	%	1.82	0.31	3.61
Oxygen	%	82.6	58.9	86.9
Nitrogen	%	0.18	0.03	0.34
Hydrogen	%	10.8	9.67	11.45
Phosphorus	ppm	266	40	560
Organics --				
Benzene	mg/kg	1.9	ND	6.5
Chlorobenzene	mg/kg	ND	ND	ND
Toluene	mg/kg	13	ND	77
Metals --				
Arsenic (As)	mg/kg	0.45	ND	0.52
Barium (Ba)	mg/kg	24.6	1.56	110
Cadmium (Cd)	mg/kg	ND	ND	ND
Chromium (Cr)	mg/kg	2.61	ND	8.64
Lead (Pb)	mg/kg	2.56	ND	3.33
Mercury (Hg)	mg/kg	0.78	0.07	3.7
Selenium (Se)	mg/kg	8.1	ND	14.8
Silver (Ag)	mg/kg	6.4	0.59	39

3.0 OVERVIEW OF HRA APPROACH

The HRA will be conducted using the recent California EPA guidance document "Air Toxics Hot Spots Program Risk Assessment Guidelines" (CalEPA, 2003) in accordance with a recommendation from California EPA's Department of Toxic Substances Control (personal communication with Mr. Dave Berry of the HERD group at DTSC; January, 2005). In addition to the guidance document, California EPA also provides the software for conducting the air emissions risk calculations. Risk calculations will be conducted using the Hot Spots Analysis and Reporting Program (HARP) software. The HARP software package consists of three modules that include: 1) the Emissions Inventory Database Module, 2) the Air Dispersion Modeling Module, and 3) the Risk Analysis and Mapping Module.

This guidance document uses a tiered approach to risk assessment. Tier 1 is a standard point-estimate approach using the recommended exposure parameters provided in the guideline document. Tier 2 allows the use of site-specific information to modify some of the point estimates. Tier 3 uses a stochastic approach to exposure assessment and is used with data distributions presented in the guidance document. Tier 4 is also a stochastic approach but allows for use of site-specific distributions. As required under the Hot Spots program, the Tier 1 evaluation will be completed initially. Depending on the results of the Tier 1 evaluation, additional site-specific information will be included in a further evaluation using one or more of the subsequent tiers.

It is assumed that the actual air dispersion and risk assessment modeling using the HARP software will be provided electronically to the reviewing agency. The report and summary of the data will be provided on paper.

The following sections will describe in more detail the methodologies proposed for: determining emissions information; performing air dispersion modeling; calculating exposure assessments; determining dose-response assessments; and performing risk characterization.

4.0 EMISSIONS INFORMATION

4.1 Emission Sources

The permitted units at the facility include the three CO Boilers and Tank 12038. A former hazardous waste unit, the Biotreater, no longer receives hazardous waste and DTSC previously agreed to a delay of closure. Similar to the previous HRA (Bechtel, 2000), Biotreater emissions will not be included in this HRA. Therefore, health risks associated with air emissions from the three CO Boilers and Tank 12038 will be calculated in the HRA.

Hazardous waste combustion in the CO Boilers results in combustion by-products being emitted from the three stacks. In addition to the stack sources, fugitive sources also release air emissions. The fugitive emission sources include the waste feed storage tank (Tank 12038), process equipment (i.e. valves, flanges, pumps, etc.) and ash handling.

4.2 Compounds of Potential Concern (COPCs)

COPCs include various compounds emitted from the facility that are evaluated quantitatively in the HRA. COPCs typically include metals, dioxins, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs). The list of compounds to be analyzed in the upcoming Trial Burn is included in Appendix A. Compounds detected in the upcoming Trial Burn will be evaluated to determine whether they have toxicity information (such as cancer slope factors and reference doses) developed by California EPA or USEPA. Detected compounds without toxicity values will be evaluated qualitatively in the HRA by discussing them in the Uncertainty Assessment section of the report. It is likely that most of the Tentatively Identified Compounds (TICs) found in the Trial Burn tests will fall into the category of compounds without USEPA-derived toxicity values.

In addition, DTSC added some nitrogenous compounds for consideration in the Trial Burn because of concerns about urea that is injected to control NO_x. Many of these compounds do not have USEPA-derived toxicity values. In subsequent discussions with DTSC, it was determined that the compounds with the highest toxic potencies and existing laboratory analytical methods would be analyzed in the Trial Burn through the SVOC laboratory method. These additional compounds are benzidine, n-nitrosodimethylamine and n-nitrosodiethylamine. If these compounds are detected in the Trial Burn, they will be evaluated in the HRA. Any additional nitrogenous compounds or other compounds reported by the analytical laboratory as a TIC will be addressed either directly if the compound has USEPA-derived toxicity values or if not, it will be addressed in the Uncertainty Assessment.

If a compound was not detected in emissions from any of the three test runs in the Trial Burn then it will not be included in the quantitative HRA. However, if a compound is detected in emissions from one or two of the test runs, it will be assumed that the emission rate from the non-detect test run(s) is one-half the detection limit. The average emission rate from the three test runs will be used in the HRA.

In a comment letter dated September 21, 2005, DTSC requested that metals be speciated in the Trial Burn so that the HRA incorporates data on individual species. This letter provided the example of nickel which can be present in different forms that have different toxicities (such as nickel carbonyl, nickel subsulfide, elemental nickel, soluble or insoluble nickel species). While it is true that different forms of metals could have different risk assessment results, such an analysis is typically beyond the scope of a trial burn risk assessment.

Stack test sampling methods and analytical testing procedures for such chemical species have not been approved by the US EPA. For example the test method determines the total metal concentration in the stack gas. In addition, there is often insufficient toxicity data on the various forms to evaluate them separately in a risk assessment. For example, CalEPA (2003) lists two toxicity values for nickel – one for nickel and nickel compounds (except nickel oxide) and one for nickel oxide. Therefore, even if different forms of nickel were identified, it would still be necessary to evaluate them using the toxicity value for nickel and nickel compounds. Also, for some metals, the fate and transport models account for transformation of the metal in the environment. For example, inorganic mercury is assumed to be taken up in fish in the form of methylmercury. This modification is incorporated into the models used to calculate uptake into food. Therefore, despite the uncertainties, it is proposed that the Trial Burn measure for total metals, since the risk assessment models generally do not differentiate between the forms of metals because of lack of necessary toxicity values.

4.3 Emission Rates

Emission rates of the COPCs will be based on the upcoming Trial Burn results. The Trial Burn evaluates normal operating conditions and provides information on long term (annual) average emission rates that are used to determine carcinogenic and chronic exposures. The Air Toxics Hot Spots Program Risk Assessment Guidelines (CalEPA, 2003) states that risk assessments should also evaluate maximum one-hour emissions for each compound; however it does not provide specific guidance on developing these maximum one-hour emissions. The approach provided in USEPA's Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities (USEPA, 1998) and also used in the previous risk assessment for this facility (Bechtel, 2000) is to assume that emissions during process upsets are 10 times greater than emissions measured in the trial burn (under normal conditions). However, USEPA (1998) states that, when available, facilities should use site-specific emissions or process data to estimate the upset factor.

The CO Boilers are equipped with an automatic waste feed cut-off system that will automatically shut-off the hazardous waste feed to each boiler based on DTSC permit specified criteria. Therefore, it is very unlikely that maximum short-term emissions could be 10 times the normal emissions. However, lacking any other guidance on this issue, the HRA will conduct a screening level assessment with the initial assumption that maximum short-term emissions are 10 times the normal emissions.

In accordance with CalEPA (2003), the estimated maximum short-term concentrations will be compared against acute Reference Exposure Levels (RELs) developed by California EPA's Office of Environmental Health Hazard Assessment. For compounds lacking acute RELs, other sources will be evaluated, such as Acute Exposure Guideline Levels (AEGLs) developed by the National Academy of Sciences. If necessary, the conservative assumption of short term emission levels will be reevaluated during the HRA process.

5.0 AIR DISPERSION MODELING

An air modeling approach similar to the approach used in the previous risk assessment (Bechtel, 2000) is proposed for this HRA.

5.1 Air Dispersion Model

The most recent version of the U.S. EPA-approved Industrial Source Complex (ISC3) air dispersion model will be used to calculate short-term and long-term ambient concentrations of compound air emissions. The region surrounding the SMR is both flat and hilly, with some portions exhibiting rural characteristics (i.e., open space, water) and others exhibiting urban characteristics (industrial and commercial areas, and some residential areas). The air emission sources associated with the CO Boilers and Tank 12038 can be characterized as point (e.g., stacks) and area emission sources (e.g., fugitives). As in the Bechtel (2000) risk assessment, the air model will be run in intermediate terrain mode and regulatory default mode.

Buildings or structures located near stacks have the potential to cause the stack plumes to mix rapidly downward, potentially resulting in high ground-level concentrations (i.e., building downwash). The dimensions of structures located at SMR will be input to the latest version of U.S. EPA's Building Profile Input Program (BPIP, version 95086) to calculate wind direction-specific building parameters for input to the air dispersion model.

The ISC3 and BPIP models are incorporated as modules within the HARP software.

5.2 Meteorological Data

Similar to the Bechtel (2000) risk assessment, one year of high quality meteorological data collected at two monitoring stations within SMR will be used. The Shell West Station is located approximately two kilometers northwest of the CO Boilers and the Shell East Station is located approximately one kilometer east of the CO Boilers. The predominant wind flow in the vicinity of the SMR is westerly, through the Carquinez Strait. However, hilly terrain located within and near the SMR can have a localized effect on the wind and can channel it in a more north-south direction. Because of its location, the Shell West Station wind measurements are representative of the predominant westerly wind flow through the Carquinez Strait. The Shell East Station data show a more frequent occurrence of winds from the north-northwesterly and southerly directions, which likely results from the hilly terrain. The Bechtel (2000) risk assessment used data from both stations to simulate plumes transported due to localized flow conditions, and plumes transported due to the predominant westerly wind flow through the Carquinez Strait. The same approach will be used for this HRA.

It is assumed that the meteorological data will be processed into air dispersion model-ready format by the BAAQMD and that the BAAQMD will use a default mixing height of 600 meters rather than upper air data collected at Oakland International Airport.

To locate the maximum risks (i.e. for cancer risk, chronic hazard and acute hazard), ISC3 will be run using 1 year of Shell West meteorological data and then 1 year of Shell East meteorological data on a coarse receptor grid; first using urban dispersion coefficients then using rural dispersion coefficient. The ISC3 results for each combination of meteorological data site and dispersion coefficients will be used by HARP to calculate the cancer risk and hazard indices on the coarse grid. The combination of meteorological data site (Shell West or Shell East) and dispersion coefficients (urban or rural) producing the highest results on the coarse grid will be used in subsequent fine grid runs. This fine grid will ensure that the location of the maximum cancer risk and hazard indices will be determined.

6.0 EXPOSURE ASSESSMENT

The exposure assessment is the process by which the type and magnitude of human exposure to COPC emissions is calculated. The exposure assessment consists of identifying receptors, identifying relevant exposure pathways for the receptors, and quantifying the COPC concentrations that could be present in the various media.

6.1 Identification of Receptors

In accordance with CalEPA (2003), a minimum of three receptors are evaluated; these are:

- 1) the Point of Maximum Impact (PMI),
- 2) the Maximally Exposed Individual Resident (MEIR), and
- 3) the Maximally Exposed Individual Worker (MEIW).

The PMI is defined as the receptor point with the highest acute, chronic or cancer health impacts outside the facility boundary. The MEIR is defined as the existing off-site residence with the highest acute, chronic or cancer health impacts. The MEIW is defined as the highest acute, chronic, or cancer health impacts at an existing off-site workplace. If the facility emits from two or more stacks, the acute, chronic, and cancer health impacts for the PMI, MEIR and MEIW may be located at different physical locations. It is common that the location of maximum deposition could be different from the location of maximum air concentration. In that case, the HRA will assume that the same receptor still receives all these impacts, or multiple receptor locations will be evaluated.

6.2 Identification of Exposure Pathways

The exposure pathways evaluated depend on the specific COPC and specific receptor. CalEPA (2003) states that the inhalation pathway is evaluated for all COPCs. A small subset of COPCs is subject to deposition on to the soil, plants, and water bodies. These COPCs need to be evaluated by the appropriate noninhalation pathways, as well as by the inhalation pathway. These COPCs include SVOCs and metals.

For the resident receptor, relevant exposure pathways are:

- Inhalation
- Soil ingestion and dermal contact
- Plant ingestion
- Drinking water ingestion
- Fish ingestion
- Mother's milk ingestion (specifically for dioxins)

Beef, dairy, poultry, and egg ingestion are not viable exposure routes because there are no significant sources of these operations impacted by the CO Boiler emissions (Bechtel, 2000). Some of the exposure pathways that are proposed to be evaluated quantitatively are unlikely to be significant risk issues; however, they can not be ruled out and will be addressed according to CalEPA (2003). It is assumed that off-site residents could have backyard gardens, which could receive depositions of SVOCs and metals emitted from the facility. The default equations listed in CalEPA (2003) will be used to estimate uptake into plants through direct deposition onto the surface and absorption through the root system.

The drinking water ingestion pathway was also evaluated in the previous risk assessment (Bechtel, 2000), which considered the Martinez reservoir for this pathway. This reservoir has the capacity for 270 acre-feet of water and is located approximately 0.2 miles south of the nearest SMR property boundary and about 0.5 miles southeast of the CO Boilers. The Martinez Reservoir is fed by the Contra Costa Canal, a 48 mile long water conveyance managed by the Contra Costa Water District (CCWD). Water from the Martinez Reservoir is pumped to the city of Martinez Water Treatment Plant. After treatment the water is supplied to the residents of Martinez as potable water. The default equations listed in CalEPA (2003) will be used to estimate deposition onto the Martinez Reservoir.

Similar to the previous risk assessment (Bechtel, 2000), the HRA will consider that people living in the area could consume fish from the Carquinez Strait. While it is unlikely that emissions from the CO Boilers could result in fish tissue concentrations significantly higher than existing background levels, this pathway cannot be ruled out and will be evaluated in accordance with CalEPA (2003). The Carquinez Strait feeds water from Suisun Bay to the San Francisco Bay and is a part of the San Francisco Bay-Delta Estuary Watershed, which receives flows from the Sacramento and San Joaquin river delta system and empties into the Pacific Ocean. The State Water Resources Control Board (SWRCB) has designated beneficial uses of the Carquinez Strait as industrial service supply, a shipping waterway, recreation, commercial fishing, migration of aquatic organisms, spawning and fish reproduction, and an estuarine and wildlife habitat. CalEPA (2003) provides default equations to estimate facility deposition onto a surface water body, and compound-specific bioaccumulation factors to estimate compound concentrations in fish tissue resulting from estimated concentrations in surface water.

In accordance with CalEPA (2003), relevant exposure pathways for the worker receptor are:

- Inhalation
- Soil ingestion and dermal contact

The noninhalation pathways will be evaluated only for the multipathway COPCs, such as SVOCs and metals.

6.3 Exposure Models

For the risk calculations, it is necessary to estimate concentrations in environmental media including air, soil, water, plants and animal products. The HARP software will be used to estimate these concentrations, and conduct risk calculations for the selected receptors. The Tier 1 evaluation will be conducted using the default parameter values presented in the HARP software. If additional tiers are conducted, then specific parameters will be modified to reflect site-specific considerations.

7.0 DOSE-RESPONSE ASSESSMENT

Dose-response assessment describes the quantitative relationship between the amount of exposure to a compound (the dose) and the occurrence of an adverse health impact (the response). Under CalEPA guidance, the dose-response information for noncarcinogens is presented in the form of Reference Exposure Levels (RELs). RELs are concentrations or doses at or below which adverse effects are not likely to occur following specified exposure conditions. Chronic RELs are used for compounds with the potential for chronic noncancer health effects. Acute RELs (inhalation only) are used for compounds with the potential for acute noncancer health effects.

For potential carcinogens, the dose-response value is the cancer slope factor, which describes the potential risk of developing cancer per unit of average daily dose over a 70-year lifetime. Inhalation and oral cancer slope factors have been determined by CalEPA's Office of Environmental Health Hazard Assessment (OEHHA) or by U.S. EPA and endorsed by OEHHA.

The dose-response values incorporated in the HARP software will be compared against OEHHA's latest values to ensure that the most recent dose-response values are being used in the HRA. For any COPCs lacking OEHHA values, values derived by USEPA will be used.

8.0 RISK CHARACTERIZATION

The risk characterization involves combining information developed through the exposure assessment with dose-response values to quantify the cancer and noncancer health impacts. Risk characterization results will include the following:

- Chronic cancer and noncancer health impacts and acute inhalation effects at the PMI, MEIR and MEIW locations.
- Estimates of population exposure for potential cancer risk, and noncancer acute and chronic health impacts.

The HARP software will be used to calculate risk estimates for the various specific receptor locations. The HARP software will also be used to calculate population-level risk estimates for cancer and noncancer effects. As stated in CalEPA (2003), population-level cancer risk estimates can be calculated as cancer burden estimates (calculated by multiplying the number of people exposed by the cancer risk at the MEIR) or estimates of the number of people exposed at specific cancer risk levels. The HRA will use the approach of estimating the number of people exposed at various cancer risk levels. CalEPA (2003) states that this approach provides a much easier way to interpret results when compared to cancer burden estimates. The latest available census results will be used to determine the population estimates. A noncancer population estimate of the number of people exposed to acute and chronic noncancer Hazard Indices exceeding 1 will also be presented.

8.1 Uncertainty Analysis

An uncertainty analysis will be included in the Risk Characterization section of the HRA. This section will discuss uncertainties in the toxicity data, exposure estimates and risk characterization results. This section will help to put the risk estimates into perspective.

8.2 Discussion of Potential Ecological Impacts

Similar to the previous risk assessment (Bechtel, 2000), a screening level ecological risk assessment will be conducted. The maximum modeled compound concentrations in various media will be compared to acceptable screening-level concentrations. In the previous risk assessment, the modeled compound concentrations were found to be well below the screening levels.

9.0 REFERENCES

Bechtel. 2000. Martinez Refining Company. CO Boiler Health Risk Assessment. Bechtel Corporation, San Francisco, California. June 2000.

CalEPA. 2003. Air Toxics Hot Spots Program Risk Assessment Guidelines – The Air Toxics Hot Spots Program Guidance Manual for Preparation of Health Risk Assessments. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. August 2003.

ENSR. 2005. Trial Burn Plan for CO Boiler Units 1, 2 and 3"; Revision 1; Document No. 05975-140-500; November, 2005.

Shell Oil Company. 1989. Environmental Analysis of The Combustion of Wastewater Treatment Sludge at The Shell Oil Company Martinez Manufacturing Complex (Volumes I and II). Prepared for the Shell Oil Company by Radian Corporation. October 16, 1989 [as cited in Bechtel, 2000].

U.S. EPA, 1998. Human Health Risk Assessment Protocol for Hazardous Waste combustion Facilities. Office of Solid Waste and Emergency Response EPA-530-D-98-001A, July 1998.

Appendix A

Compounds to be Analyzed in the Upcoming Trial Burn

STL Knoxville VOST Expanded List (values as of 05/21/04)								
Compound	RL	Units	MDL	Units	QA/QC	LCL	UCL	RPD
Acetone	0.1	µg	0.06	µg				
Acrylonitrile	0.50	µg	0.098	µg				
Benzene	0.025	µg	0.0043	µg	C	69	130	25
Bromobenzene	0.025	µg	0.0047	µg				
Bromochloromethane	0.025	µg	0.0055	µg				
Bromodichloromethane	0.025	µg	0.0044	µg				
Bromoform	0.025	µg	0.0065	µg				
Bromomethane	0.05	µg	0.0078	µg				
2-Butanone	0.1	µg	0.032	µg				
n-Butylbenzene	0.025	µg	0.0077	µg				
sec-Butylbenzene	0.025	µg	0.0096	µg				
tert-Butylbenzene	0.025	µg	0.0089	µg				
Carbon disulfide	0.025	µg	0.0042	µg				
Carbon tetrachloride	0.025	µg	0.0034	µg				
Chlorobenzene	0.025	µg	0.0043	µg	C	58	116	25
Chlorodibromomethane	0.025	µg	0.0038	µg				
Chloroethane	0.05	µg	0.0039	µg				
Chloroform	0.025	µg	0.0046	µg				
Chloromethane	0.05	µg	0.006	µg				
2-Chlorotoluene	0.025	µg	0.0054	µg				
4-Chlorotoluene	0.025	µg	0.0057	µg				
1,2-Dibromo-3-chloropropane	0.05	µg	0.016	µg				
1,2-Dibromoethane	0.025	µg	0.0039	µg				
Dibromomethane	0.025	µg	0.0064	µg				
1,2-Dichlorobenzene	0.025	µg	0.0059	µg				
1,3-Dichlorobenzene	0.025	µg	0.0064	µg				
1,4-Dichlorobenzene	0.025	µg	0.0074	µg				
Dichlorodifluoromethane	0.025	µg	0.0052	µg				
1,1-Dichloroethane	0.025	µg	0.0034	µg				
1,2-Dichloroethane	0.025	µg	0.0048	µg				
cis-1,2-Dichloroethene	0.025	µg	0.005	µg				
trans-1,2-Dichloroethene	0.025	µg	0.0038	µg				
1,1-Dichloroethene	0.025	µg	0.0057	µg	C	63	150	25
1,2-Dichloropropane	0.025	µg	0.0045	µg				
1,3-Dichloropropane	0.025	µg	0.0071	µg				
2,2-Dichloropropane	0.025	µg	0.0034	µg				
cis-1,3-Dichloropropene	0.025	µg	0.0039	µg				
trans-1,3-Dichloropropene	0.025	µg	0.0039	µg				
1,1-Dichloropropene	0.025	µg	0.0042	µg				
Ethylbenzene	0.025	µg	0.0032	µg				
Hexachlorobutadiene	0.025	µg	0.0041	µg				
2-Hexanone	0.1	µg	0.018	µg				

STL Knoxville VOST Expanded List (values as of 05/21/04)								
Compound	RL	Units	MDL	Units	QA/QC	LCL	UCL	RPD
Isopropylbenzene	0.025	µg	0.0058	µg				
p-Isopropyltoluene	0.025	µg	0.0085	µg				
Methylene chloride	0.025	µg	0.012	µg				
4-Methyl-2-pentanone	0.1	µg	0.029	µg				
n-Propylbenzene	0.025	µg	0.0054	µg				
Styrene	0.025	µg	0.0049	µg				
1,1,1,2-Tetrachloroethane	0.025	µg	0.0046	µg				
1,1,2,2-Tetrachloroethane	0.025	µg	0.0067	µg				
Tetrachloroethene	0.025	µg	0.0044	µg				
Toluene	0.025	µg	0.0027	µg	C	64	128	25
1,2,3-Trichlorobenzene	0.025	µg	0.0056	µg				
1,2,4-Trichlorobenzene	0.025	µg	0.0066	µg				
1,1,1-Trichloroethane	0.025	µg	0.0051	µg				
1,1,2-Trichloroethane	0.025	µg	0.0056	µg				
Trichloroethene	0.025	µg	0.0099	µg	C	72	150	25
Trichlorofluoromethane	0.05	µg	0.008	µg				
1,2,3-Trichloropropane	0.025	µg	0.0099	µg				
1,2,4-Trimethylbenzene	0.025	µg	0.0063	µg				
1,3,5-Trimethylbenzene	0.025	µg	0.0074	µg				
Vinyl chloride	0.025	µg	0.0032	µg				
m-Xylene & p-Xylene	0.05	µg	0.0072	µg				
o-Xylene	0.025	µg	0.0053	µg				
Bromofluorobenzene					S	50	125	0
1,2-Dichloroethane-d4					S	50	134	0
Toluene-d8					S	57	127	0
Dibromofluoromethane					S	50	134	0

STL = Severn Trent Laboratories

VOST = volatile organic sampling train

RL = Reporting Limit – this reflects the low calibration point of the calibration curve and the amount per thermal desorption.

MDL = Method Detection Limit – this is the lowest amount the laboratory will report down to.

QA/QC = Quality Assurance/Quality Control Parameter

LCL = Lower Control Limit for acceptable recovery

UCL = Upper Control Limit for acceptable recovery

RPD = relative percent difference

µg = micrograms

C = Matrix Spike or Laboratory Control Standard compound

S = Surrogate

STL Knoxville SVOC Combined Train Expanded List (values as of 05/21/04)									
Compound	RL	Units	MDL	Units	QA/QC	LCL	UCL	RPD	
Benzidine	10	µg	1.8	µg					
bis(2-Chloroethoxy)methane	10	µg	1.8	µg					
bis(2-Chloroethyl) ether	10	µg	2	µg					
bis(2-Chloroisopropyl) ether	10	µg	2.4	µg					
bis(2-Ethylhexyl) phthalate	20	µg	14	µg					
4-Bromophenyl phenyl ether	10	µg	1.6	µg					
Butyl benzyl phthalate	10	µg	2.6	µg					
4-Chloroaniline	20	µg	10	µg					
4-Chloro-3-methylphenol	10	µg	4.1	µg	C	63	114	31	
2-Chloronaphthalene	10	µg	1.5	µg					
2-Chlorophenol	10	µg	2.1	µg	C	59	108	39	
4-Chlorophenyl phenyl ether	10	µg	2.2	µg					
Di-n-butyl phthalate	20	µg	12	µg					
1,2-Dichlorobenzene	10	µg	2	µg					
1,3-Dichlorobenzene	10	µg	2.3	µg					
1,4-Dichlorobenzene	10	µg	2.4	µg	C	43	99	36	
3,3'-Dichlorobenzidine	50	µg	13	µg					
2,4-Dichlorophenol	10	µg	2.9	µg					
Diethyl phthalate	10	µg	2.8	µg					
2,4-Dimethylphenol	10	µg	9.8	µg					
Dimethyl phthalate	10	µg	1.6	µg					
4,6-Dinitro-2-methylphenol	50	µg	14	µg					
2,4-Dinitrophenol	50	µg	29	µg					
2,4-Dinitrotoluene	10	µg	3.1	µg	C	71	122	33	
2,6-Dinitrotoluene	10	µg	2.6	µg					
Di-n-octyl phthalate	10	µg	3.6	µg					
Hexachlorobenzene	10	µg	2.1	µg					
Hexachlorobutadiene	10	µg	2.9	µg					
Hexachlorocyclopentadiene	50	µg	23	µg					
Hexachloroethane	10	µg	3.8	µg					
Isophorone	10	µg	1.8	µg					
2-Methylphenol	10	µg	6.1	µg					
2-Nitroaniline	50	µg	2.2	µg					
3-Nitroaniline	50	µg	7.6	µg					
4-Nitroaniline	50	µg	5.8	µg					
Nitrobenzene	10	µg	1.9	µg					
2-Nitrophenol	10	µg	4.7	µg					
4-Nitrophenol	50	µg	8.1	µg	C	47	134	26	
N-Nitrosodiethylamine	10	µg	2	µg					
N-Nitrosodimethylamine	10	µg	2	µg					
N-Nitrosodiphenylamine	10	µg	2	µg					

STL Knoxville SVOC Combined Train Expanded List (values as of 05/21/04)									
Compound	RL	Units	MDL	Units	QA/QC	LCL	UCL	RPD	
N-Nitrosodi-n-propylamine	10	µg	2.1	µg	C	44	119	38	
Pentachlorophenol	100	µg	51	µg	C	63	123	26	
Phenol	10	µg	2.8	µg	C	58	114	36	
1,2,4-Trichlorobenzene	10	µg	2.1	µg	C	59	111	33	
2,4,5-Trichlorophenol	10	µg	4.4	µg					
2,4,6-Trichlorophenol	10	µg	3.1	µg					
2-Fluorobiphenyl					S	34	115		
2-Fluorophenol					S	19	100		
2,4,6-Tribromophenol					S	33	130		
Nitrobenzene-d ₅					S	35	122		
Phenol-d ₅					S	15	124		
Terphenyl-d ₁₄					S	28	132		
¹³ C ₆ -Naphthalene					F	50	150		

STL = Severn Trent Laboratories

SVOC = semi-volatile organic compound

RL = Reporting Limit – this reflects the low calibration point of the calibration curve and the amount per thermal desorption.

MDL = Method Detection Limit – this is the lowest amount the laboratory will report down to.

QA/QC = Quality Assurance/Quality Control Parameter

LCL = Lower Control Limit for acceptable recovery

UCL = Upper Control Limit for acceptable recovery

RPD = relative percent difference

µg = micrograms

C = Matrix Spike or Laboratory Control Standard compound

S = Surrogate

F = Field Surrogate (pre-spiked onto XAD prior to shipping to the field)

TARGET PCDDs/PCDFS and PAHs

SHELL OIL PRODUCTS US
Martinez, California

2006 RCRA TRIAL BURN
EPA Method 0023A / 0010 Sampling Train

Target PAH Compounds	Target PCDD/PCDF Congeners
<u>Noncarcinogenic PAHs:</u>	<u>Chlorinated Dioxins:</u>
Naphthalene	2,3,7,8-TCDD
2-Methylnaphthalene	1,2,3,7,8-PeCDD
Acenaphthylene	1,2,3,4,7,8-HxCDD
Acenaphthene	1,2,3,6,7,8-HxCDD
Fluorene	1,2,3,7,8,9-HxCDD
Phenanthrene	1,2,3,4,6,7,8-HpCDD
Anthracene	OCDD
Fluoranthene	
Pyrene	<u>Chlorinated Furans:</u>
Benzo(e)pyrene	2,3,7,8-TCDF
Perylene	1,2,3,7,8-PeCDF
Benzo(g,h,i)perylene	2,3,4,7,8-PeCDF
	1,2,3,4,7,8-HxCDF
<u>Carcinogenic PAHs:</u>	1,2,3,6,7,8-HxCDF
Benzo(a)anthracene	2,3,4,6,7,8-HxCDF
Chrysene	1,2,3,7,8,9-HxCDF
Benzo(b)fluoranthene	1,2,3,4,6,7,8-HpCDF
Benzo(k)fluoranthene	1,2,3,4,7,8,9-HpCDF
Benzo(a)pyrene	OCDF
Indeno(1,2,3-c,d)pyrene	
Dibenz(a,h)anthracene	

TARGET Carbonyls and Inorganics

**SHELL OIL PRODUCTS US
Martinez, California**

2006 RCRA TRIAL BURN

<u>EPA Method 0050 Sampling Train – Inorganics:</u>	<u>EPA Method 0011 Sampling Train – Carbonyls:</u>
--	---

Particulate Matter

Acetaldehyde

Hydrogen Chloride

Crotonaldehyde

Chlorine

Formaldehyde

Ammonia

Propionaldehyde

EPA Method 0060 Sampling Train – Metals:

EPA Method 0061 Sampling Train – Metals:

Aluminum

Hexavalent Chromium

Antimony

Arsenic

Barium

Beryllium

Cadmium

Chromium (Total)

Cobalt

Copper

Lead

Manganese

Mercury

Nickel

Selenium

Silver

Thallium

Vanadium

Zinc